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***Central Eurasia:  
Chemistry***

# Science & Technology CENTRAL EURASIA: Chemistry

JPRS-UCH-93-007

## CONTENTS

17 June 1993

### CATALYSIS

A Kinetic Model of Chemical and Physical Processes During Pulse Initiation. Conversion of Freon-22 Under Conditions of Laser Heating <i>[N. Yu. Ignatyeva, Yu. N. Zhitnev, et al.; KINETIKA I KATALIZ, Vol 34 No 2, Apr 93]</i>	1
Thermal Decomposition of Diethyltelluride in the Gaseous Phase <i>[G. G. Devyatikh, I. S. Zaslonsko, et al.; KINETIKA I KATALIZ, Vol 34 No 2, Apr 93]</i>	1
Quantum Yield and Rate of Photoinduced Oxidation of Saturated Hydrocarbons by Polyoxotungstates in Solutions <i>[V. P. Tretyakov; KINETIKA I KATALIZ, Vol 34 No 2, Apr 93]</i>	1
Reactions in Liquid Hydrogen Chloride. 1. Chlorination of Aromatic Hydrocarbons <i>[V. V. Smirnov, T. N. Rostovshchikova, et al.; KINETIKA I KATALIZ, Vol 34 No 2, Apr 93]</i>	2
An Investigation of the Adsorption Properties of Platinum in Relation to the Substances Participating in the Reaction of the Deep Oxidation of Ethanol <i>[V. Yu. Konyukhov, V. E. Chitava, et al.; KINETIKA I KATALIZ, Vol 34 No 2, Apr 93]</i>	2

### ELECTROCHEMISTRY

Metal and Metal-Modified Electrocatalysts <i>[B. I. Podlovchenko, A. G. Pshenichnikov, et al.; ELEKTROKHIMIYA, Vol 29 No 4, Apr 93]</i>	3
Bioelectrocatalysis: Problems and Prospects <i>[V. A. Bogdanovskaya; ELEKTROKHIMIYA, Vol 29 No 4, Apr 93]</i>	3
Electrocatalysts for Electrochemical Devices <i>[N. V. Korovin, E. V. Kasatkin; ELEKTROKHIMIYA, Vol 29 No 4, Apr 93]</i>	4
The Production and Properties of Palladium Deposits on Carbon Fabric <i>[Shigan Lu, Ye. A. Kolyadko, et al.; ELEKTROKHIMIYA, Vol 29 No 4, Apr 93]</i>	5
Intensifying Process of Hydrogen Transfer to Palladium Membrane <i>[I. I. Kolesnichenko, A. A. Michri, et al.; ELEKTROKHIMIYA, Vol 29 No 4, Apr 93]</i>	5

### MATERIALS RESEARCH

The Electron Heat Capacity of Superconductors With an Intermediate Link <i>[A. P. Zhernov, E. P. Chulkov; SVERKHPROVODIMOST: FIZIKA, KHIMIYA, TEKHNIKA, Vol 6 No 1, Jan 93]</i>	6
Paramagnetism and Superconductivity in the Hubbard Model With Strong Repulsion <i>[R. O. Zaytsev; SVERKHPROVODIMOST: FIZIKA, KHIMIYA, TEKHNIKA, Vol 6 No 1, Jan 93]</i>	6
Possible Nature of the Electron Spectrum and Conductivity of Doped Fullerite <i>[M. A. Ivanov, V. M. Loktev, et al.; SVERKHPROVODIMOST: FIZIKA, KHIMIYA, TEKHNIKA, Vol 6 No 1, Jan 93]</i>	6
Raman Scattering of Light on Phonons in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ Crystals With Selective Substitution of Isotopes <i>[Ye. Ya. Sherman; SVERKHPROVODIMOST: FIZIKA, KHIMIYA, TEKHNIKA, Vol 6 No 1, Jan 93]</i>	7
Optical and Electrical Properties of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ Monocrystals <i>[L. V. Nomerovannaya, A. A. Makhnev, et al.; SVERKHPROVODIMOST: FIZIKA, KHIMIYA, TEKHNIKA, Vol 6 No 1, Jan 93]</i>	7
Distinctive Features of the Josephson Effect in a Y-Ba-Cu-O Bridge in Magnetic and Microwave Fields <i>[M. A. Zelikman, A. S. Katkov, et al.; SVERKHPROVODIMOST: FIZIKA, KHIMIYA, TEKHNIKA, Vol 6 No 1, Jan 93]</i>	7
Structural Instability and Transport Properties in the System $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ <i>[Yu. S. Bulyshev, S. V. Serykh, et al.; SVERKHPROVODIMOST: FIZIKA, KHIMIYA, TEKHNIKA, Vol 6 No 1, Jan 93]</i>	8
Charge and Energy Distributions of Particles Sputtered From Y-Ba-Cu-O and Bi-Sr-Ca-Cu-O High-Temperature Superconductors <i>[A. B. Popov, S. B. Kablukov, et al.; SVERKHPROVODIMOST: FIZIKA, KHIMIYA, TEKHNIKA, Vol 6 No 1, Jan 93]</i>	8

Characteristic Features of the Laser Desorption of Oxygen From a $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ Monocrystal Near $T_c$ <i>[P. O. Artamonov, A. A. Lisachenko; SVERKHPROVODIMOST: FIZIKA, KHIMIYA, TEKHNIKA, Vol 6 No 1, Jan 93]</i>	9
Ohmic Contacts to a $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ Oxide Superconductor Produced by the Silver Foil Electroexplosion Method <i>[O. N. Alifertsev, V. P. Snesarevskiy; SVERKHPROVODIMOST: FIZIKA, KHIMIYA, TEKHNIKA, Vol 6 No 1, Jan 93]</i>	9
Electrolytic Oxygen Saturation of Y-Ba-Cu-O Ceramics in Solutions and Their Resistometric Characteristics <i>[V. D. Kalugin, V. N. Yasko, et al.; SVERKHPROVODIMOST: FIZIKA, KHIMIYA, TEKHNIKA, Vol 6 No 1, Jan 93]</i>	9
Phase Relationship in a $\text{BaCu}_3\text{O}_4$ - $\text{Y}_2\text{Cu}_3\text{O}_6$ Polythermal Section and Projection of the Liquidus Surface of the System Y-Ba-Cu-O <i>[A. I. Sechnoy, G. A. Mikirticheva, et al.; SVERKHPROVODIMOST: FIZIKA, KHIMIYA, TEKHNIKA, Vol 6 No 1, Jan 93]</i>	9
The Reaction of $\text{YBa}_2\text{Cu}_3\text{O}_6$ With Iodine. 1. Phase Composition of Reaction Products <i>[A. P. Nemudryy, S. S. Shatskaya, et al.; SVERKHPROVODIMOST: FIZIKA, KHIMIYA, TEKHNIKA, Vol 6 No 1, Jan 93]</i>	10
The Reaction of $\text{YBa}_2\text{Cu}_3\text{O}_6$ With Iodine. 2. The Effect of Iodine on the Superconducting Characteristics of Yttrium-Barium Cuprite <i>[A. P. Nemudryy, I. I. Gaynutdinov, et al.; SVERKHPROVODIMOST: FIZIKA, KHIMIYA, TEKHNIKA, Vol 6 No 1, Jan 93]</i>	10
The State of Silver in $\text{YBaCuO}/\text{Ag}$ Composites <i>[S. Yu. Sumarokov, N. I. Shevtsov, et al.; SVERKHPROVODIMOST: FIZIKA, KHIMIYA, TEKHNIKA, Vol 6 No 1, Jan 93]</i>	11

## ORGANOMETALLIC COMPOUNDS

Fullerenes—A New Form of Carbon <i>[Mark Yefimovich Volpin; VESTNIK ROSSIYSKOY AKADEMII NAUK, No 10, Oct 92]</i>	12
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**A Kinetic Model of Chemical and Physical Processes During Pulse Initiation. Conversion of Freon-22 Under Conditions of Laser Heating**

937M0146A Moscow KINETIKA I KATALIZ  
in Russian Vol 34 No 2, Apr 93 pp 207-212

[Article by N. Yu. Ignatyeva, Yu. N. Zhitnev, V. V. Timofeyev, Ye. A. Tveritinova, and A. V. Zakharchenko, Chemistry Department, Moscow State University imeni M. V. Lomonosov; UDC 541.144.8:541.127:541.124.2:547.412.126.23]

[Abstract] The method of pulsed infrared initiation of chemical transformations is examined theoretically. A mathematical model is proposed that describes the set of physical and chemical processes occurring in the post-pulse period, i.e., the change in the temperature and concentration fields throughout the volume of the chemical reactor that occurs over time. Next, experiments were conducted to examine the decomposition of  $\text{CHClF}_2$  in the presence of a sensitizer subjected to a TEA  $\text{CO}_2$  laser (multimode operation; wavelength, 10.6 mm). A  $\text{CO}_2:\text{N}_2:\text{He:D}_2$  (in a 1:1:4:1 ratio) was used. Type OSIM-1 and IMO-2N meters were used to measure the laser pulse energy and power. The laser beam measured 20 x 20 mm, and a 7.5-mm diaphragm was used to separate the most homogeneous part of the infrared beam for total irradiation of the reaction space. The reaction cell measured 7.5 mm in diameter and 7.2 cm in length. The absorbed energy was determined from the difference of the energies entering the cell and passed through it. Pulsed heating with repeated multiple irradiation (pulse repetition frequency, 0.2 Hz) of the mixture was used to study the deep conversion of the  $\text{CHClF}_2$ . The composition of the products was found to depend on laser pyrolysis conditions. Under conditions of pulsed laser pyrolysis, the  $\text{C}_{\text{F}4}$  yield amounted to 95 percent with virtually complete conversion of the starting Freon. The data obtained in the experiment were consistent with those calculated on the basis of a model of the results. Figures 3; references 30: 16 Russian, 14 Western.

**Thermal Decomposition of Diethyltelluride in the Gaseous Phase**

937M0146B Moscow KINETIKA I KATALIZ  
in Russian Vol 34 No 2, Apr 93 pp 213-217

[Article by G. G. Devyatkh, I. S. Zaslonsko, V. N. Smirnov, A. N. Moiseyev, V. N. Votintsev, and A. M. Tereza, Chemical Physics Institute imeni N. N. Semenov, Russian Academy of Sciences, Moscow, and High-Purity Materials Chemistry Institute, Russian Academy of Sciences, Nizhny Novgorod; UDC 541.127: 542.921.4:547.269.9:533.951]

[Abstract] A study examined the thermal decomposition of diethyltelluride in shock waves at temperatures from 900 to 1,100 K with a total gas density of  $5 \times 10^{-6}$  mol/cm<sup>3</sup>. The course of the reaction was monitored by the change in optical density in a continuous spectrum at a wavelength of 250 nm (absorption by diethyltelluride molecules) and by the method of atomic absorption spectroscopy on a resonance line with a wavelength of 225.9 nm based on registration of atomic tellurium. The concentration of diethyltelluride in the shock tube was determined from the known extinction coefficient value. A modulation disk rotating at a speed of 3,000 rpm was used to measure the initial intensity of absorption in the empty shock tube. Mixtures containing 0.15 percent starting composition in argon were used in the experiments measuring the rate of diethyltelluride decomposition. When the Te atoms were registered, a concentration of 15 ppm diethyltelluride in argon was used. The rate constant measurements based on the starting substance and yield of tellurium atoms were consistent with one another. This fact was taken as an indication that the breaking of the first bond is the limiting stage of the decomposition. The study results were compared with those calculated on the basis of the PPKM [not further identified] theory, and an expression was derived for calculating the rate constant of the thermal decomposition of diethyltelluride under low and high pressures. A model consisting of 17 reactions (but not including the effect of heterogeneous reactions) involved in the decomposition of diethyltelluride is presented. Figures 2, table 1; references 17: 6 Russian, 11 Western.

**Quantum Yield and Rate of Photoinduced Oxidation of Saturated Hydrocarbons by Polyoxotungstates in Solutions**

937M0146C Moscow KINETIKA I KATALIZ  
in Russian Vol 34 No 2, Apr 93 pp 227-229

[Article by V. P. Tretyakov, Physical-Organic and Coal Chemistry Institute imeni L. M. Litvinenko, Ukraine Academy of Sciences, Donetsk; UDC 541.124-145: 541.14:547.21:549.76]

[Abstract] Expressions have been derived for the quantum yield ( $\phi$ ) and rate ( $W$ ) of photoinduced oxidation of saturated hydrocarbons by polyoxotungstates in solutions. The expressions were then used to analyze the results of an experiment involving the photooxidation of cyclooctane by  $\text{W}_{10}\text{O}_{32}^{4-}$  ions (1.8 mM) in acetonitrile at 25°C and a wavelength of 322 nm. The analysis established that the process of photoreduction of  $\text{W}_{10}\text{O}_{32}^{4-}$  by cyclooctane in acetonitrile includes both redox-active and redox-inactive excited decaoxotungstate ions. The parameters determining the formation and consumption of excited  $\text{W}_{10}\text{O}_{32}^{4-}$  ions were calculated. Figure 1; references 13: 6 Russian, 7 Western.

**Reactions in Liquid Hydrogen Chloride. 1.**  
**Chlorination of Aromatic Hydrocarbons**

937M0146D Moscow KINETIKA I KATALIZ  
 in Russian Vol 34 No 2, Apr 93 pp 234-236

[Article by V. V. Smirnov, T. N. Rostovshchikova, I. G. Tarkhanova, I. N. Novikov, V. B. Barabash, and I. A. Nasyr, Chemistry Department, Moscow State University imeni M. V. Lomonosov; UDC 541.124-14:542.944.1:547.532]

[Abstract] A study examined the substitution chlorination of aromatic hydrocarbons in a medium of liquid hydrogen chloride at temperatures of 170 to 230 K under ordinary pressure in the absence of any metal compounds. The composition of the reaction products was determined by gas-liquid chromatography and nuclear magnetic resonance [NMR] spectroscopy by interrupting the reaction at specified depths of transformation and after complete consumption of the chlorine. The initial concentrations of the reaction components were as follows: HCl, 0.5 to 31.5 M; aromatic hydrocarbons, 7.2 to 0.2 M; and Cl<sub>2</sub>, 0.004 to 6.8 M. To make it possible to determine the make-up and yield of chlorination products at 190 to 230 K and under pressures up to 7 x 10<sup>5</sup> Pa, the reagents were condensed into thick-walled glass ampules in a vacuum unit, after which the specimens were thermostatted in special low-temperature baths for a specified time until total disappearance of the chlorine's coloration and then frozen, unsealed, and slowly heated to remove the excess hydrogen chloride. The organic residue was then analyzed by gas-liquid chromatography and NMR spectroscopy. In the absence of hydrogen chloride, no chlorination of aromatic hydrocarbons occurred in binary mixtures or solvents at 170 to 230 K. The addition of 0.5 M HCl resulted in chlorination of toluene at temperatures as low as 180 K. In liquid hydrogen chloride, alkylbenzenes reacted quantitatively with chlorine at 170-180 K for several minutes. The toluene formed a mixture of o- and n-isomers of chlorotoluene in a 3 to 3.5 ratio. Xylools and mesitylene underwent chlorination with the formation of products monochloro-substituted into the nucleus. No substitution occurred in the alkyl groups. Benzene manifested a lower reactivity (10<sup>4</sup>-fold less active than toluene) and was chlorinated effectively only at temperatures above 203 K with the formation of mainly monochlorobenzene. The

reaction rate was found to be directly proportional to the concentrations of chlorine and aromatic hydrocarbon. Increasing the hydrogen chloride concentration resulted in a sharp increase in the chlorination rate: The reaction rate increased by three orders of magnitude when liquid hydrogen chloride (30 M) was used in place of 3 M of HCl solution. The rapid chlorination of aromatic hydrocarbons was hypothesized to be associated with the catalytic effect of HCl and strong specific solvation by the medium of intermediate (ionic in nature) particles. Figures 4; references 8: 7 Russian, 1 Western.

**An Investigation of the Adsorption Properties of Platinum in Relation to the Substances Participating in the Reaction of the Deep Oxidation of Ethanol**

937M0146E Moscow KINETIKA I KATALIZ  
 in Russian Vol 34 No 2, Apr 93 pp 319-320

[Article by V. Yu. Konyukhov, V. E. Chitava, and V. A. Naumov, Moscow Polygraphy Institute; UDC 542.943.7:547.262:546.92:541.183]

[Abstract] Gas adsorption chromatography was used to study the adsorption of C<sub>2</sub>H<sub>5</sub>OH, CH<sub>3</sub>CHO, CH<sub>3</sub>COOH, H<sub>2</sub>O, and CO<sub>2</sub>. A platinum catalyst on a copolymer of divinylbenzene and styrene (with the platinum amounting to 16 percent of the carrier's mass) was prepared to keep the adsorption of substances on the carrier from affecting the measurement results. The yield times of the study substances on the said carrier were close to those of the nonadsorbed gas (N<sub>2</sub>). The experiments were performed at temperatures of 333 to 423 K on an LKhM-80 chromatograph, and a katharometer operated as the detector. Helium with a velocity of 30 cm<sup>3</sup>/min served as the carrier gas, and 2.05 g of catalyst was used. The adsorption isotherms plotted for C<sub>2</sub>H<sub>5</sub>OH, CH<sub>3</sub>COOH, and H<sub>2</sub>O are well described by a Brunauer-Emmett-Teller [BET] equation, with the constants  $a_{\infty}$  and C calculated by the least squares method: The mean square deviation of the calculated and experimentally obtained values of  $a$  does not exceed 5 percent. The high value of the heat of adsorption of acetaldehyde obtained in the experiments is consistent with thinking regarding the mechanism of deep oxidation of ethanol, where oxidation of adsorbed acetaldehyde is the limiting stage of the reaction. Figures 2, table 1; references: 3 (Russian).

### Metal and Metal-Modified Electrocatalysts

93M0147A Moscow ELEKTROKHIMIYA in Russian  
Vol 29 No 4, Apr 93 pp 422-432

[Article by B. I. Podlovchenko, A. G. Pshenichnikov, and A. M. Skundin, Electrochemistry Institute imeni A. N. Frumkin, Russian Academy of Sciences, Moscow, and Moscow State University imeni M. V. Lomonosov; UDC 541.135.52]

[Abstract] Despite the significant expansion of research efforts in the past decade, metals of the nickel and platinum groups still remain the main electrode materials, and hydrogen evolution, ionization, oxidation, and reduction of simple organic compounds are still the predominant electrode processes studied. Recent research has investigated the effect of a metal catalyst's surface state on its adsorption and electrocatalytic properties, the development of new methods of preparing electrocatalysts, the effectiveness of using porous catalyst layers, the functional stability of modified surfaces, and the mutual effect of an applied metal and its carrier. Several studies have, for example, confirmed that anode-cathode activation results in significant changes in both surface composition and structure. Depending on the shape of the pulses used (rectangular or triangular), their frequency, and their upper and lower potential-change bounds, it is possible to obtain either a highly scarified surface (that is tens of times rougher than the starting surface) or a primarily crystallographically oriented surface. The effect of surface faceting has been explained by the hypothesis of a difference in the kinetics of the processes of formation and reduction of oxides and dissolution and deposition of metals on various monocrystal faces. Studies involving metal monocrystals and high-vacuum technology have confirmed that the rates of selected reactions on individual faces may differ more than 10-fold. The effectiveness of promoting additives in increasing both the speed and selectivity of many reactions at high anode potentials has been shown to be largely due to strong irreversible chemisorption of the promoting additive or fragments thereof, thereby resulting in significant modification of the surface (and thus giving rise to the "memory effect"). There has also been additional confirmation of the fact that in many cases, the electrocatalytic properties of disperse structures of single-component metal electrocatalysts are very different from those of compact materials. Further research is needed to explain the ineffectiveness of using thick catalyst layers, however. The past decade has seen comparatively little research on the use of polycrystalline metal alloys as electrocatalysts. Binary systems present in skeletal catalysts (including in surface skeletal catalysts) have received increased attention, and the high corrosion resistance of amorphous alloys has been confirmed in several studies. The implantation of metals with a rather high hydrogen-evolution overvoltage (iron, copper, zinc, etc.) with ions of platinum-group metals has been shown to result in a significant acceleration of the hydrogen evolution reaction. Cases of deviations from this general rule have also been demonstrated,

however. Despite somewhat of a decrease in interest in systems with adatoms in the past 5-7 years, the problems of the formation and electrochemical and electrocatalytic properties of adatom coatings have continued to command a great deal of attention. The activating effect of adatoms (2-3 orders of magnitude in a number of cases) has been established for a large number of systems. The nature of the electrocatalytic activity of adatoms has yet to be completely clarified, however. Electrocatalysis by adatoms has been shown to be very promising from the standpoint of strictly directed electrosynthesis and catalytic synthesis. Recent research has not resulted in any cardinal changes in thinking regarding applied electrocatalysts; however, the development of different methods and techniques for preparing stable applied electrocatalysts with a well-developed surface (especially for fuel elements with a phosphoric acid electrolyte) has continued. Significant progress has been made in the study of the electrode structure of small applied particles. The effect of hydrogen spillover in changing a substrate's properties in the presence of a metal catalyst has been confirmed in a number of works. The authors of three studies have proposed using copper and silver adatoms to determine the area of the true surface of platinum-group metals on carbon carriers. The advantages of the said technique have been confirmed by comparing the surface-area values obtained from electrochemical measurements with those calculated from x-ray data. Figures 9; references 123: 57 Russian, 66 Western.

### Bioelectrocatalysis: Problems and Prospects

93M0147B Moscow ELEKTROKHIMIYA in Russian  
Vol 29 No 4, Apr 93 pp 441-447

[Article by V. A. Bogdanovskaya, Electrochemistry Institute imeni A. N. Frumkin, Russian Academy of Sciences, Moscow; UDC 541.138]

[Abstract] The idea of using enzymes and enzyme components (amino acids and peptides) as biological catalysts in electrochemical processes developed in response to the need to create high-performance electrocatalysts. Proteins' activity in their immobilized state, their redox transformation capabilities, and the ability to accelerate electrode reactions are determined by their adsorption by the electrode surface and by their conformation. Electrochemical and radioisotope studies of the adsorption of albumin, myoglobin, laccase, peroxidase, and glucooxidase on carbon materials have shown that a large amount of protein is generally adsorbed on a preoxidized surface with a large number of oxygen-containing groups. Hydrophobic-hydrophilic and electrostatic interactions are also important. Pore structure is important: The larger the mesopore size, the higher the protein capacity. Studies of the electrochemical effects of amino acids and peptides on gold indicate that protein-surface interaction is possible at amino groups, peptide oxygen, and reactive side groups and that it occurs most effectively on a surface with oxygen-containing groups. The questions of proteins' conformation and orientation

when immobilized still remain unanswered; however, the intensive development of spectral methods of studying surfaces offer hope that the required knowledge will be forthcoming. Recent studies of redox transformations and bioelectrocatalysis under conditions of direct exchange of electrons among electrodes, active centers, and substrates have demonstrated that the redox processes observed may be classified as transformations in the proteins' active centers and that tunnel electron transfer probably occurs in the absence of direct contact between the electrode and the active center. Research on the mechanism of redox transformations of cytochrome C has enabled researchers to propose a protein redox transformation mechanism that includes conformational alterations of the protein globule associated with a change in molecule volume during the transition from an oxidized state to a reduced state and vice versa as a slow stage. Only isolated studies have been devoted to the mechanism of bioelectrocatalytic reactions proper. Most research on the electrocatalytic properties of proteins has been geared toward discovering the conditions for practical use of such catalysts, i.e., to clarify the reaction mechanism and use a biocatalyst-enzyme to design electrochemical devices such as biosensors and biofuel elements. In such cases, the bioelectrocatalytic reaction includes three stages: 1) the enzyme accelerates the reaction in the bulk of the solution; 2) the enzyme exchanges electrons with the mediator; and 3) the mediator reacts with the electrode. Research on the mechanism of bioelectrocatalysis of oxygen reduction in a laccase-oxygen system immobilized on a carbon material has resulted in kinetic parameters of the reaction for the low-polarization range, an expression for the current of the electroreduction of oxygen, and a theoretical explanation for the experimental data obtained. Two possible directions for further research in the field of bioelectrocatalysis are 1) expansion of the set of enzymes used under conditions of direct bioelectrocatalysis and 2) development of methods for direct determination of the extent of filling of the surface with immobilized protein and its orientation on the surface. Figures 6, tables 7; references 24: 18 Russian, 6 Western.

### Electrocatalysts for Electrochemical Devices

937M0147C Moscow ELEKTROKHIMIYA in Russian  
Vol 29 No 4, Apr 93 pp 448-460

[Article by N. V. Korovin and E. V. Kasatkin, Moscow Power Engineering Institute, Physical Chemistry Scientific Research Institute imeni L. Ya. Karpova, Moscow; UDC 541.13]

[Abstract] Electrocatalysts have found application in industrial electrolyzers, natural water and sewage treatment installations, chemical current sources, and electrochemical sensors. Electrocatalysts intended for use in electrochemical devices must have three things: high activity, high stability, and low cost. The following have been identified as the main ways of selecting catalysts and increasing electrode activity: selecting single-component catalysts having the optimal energy bond

with the adsorbed particle (e.g., platinum for a hydrogen electrode); modifying the material's structural properties by rendering them amorphous or by ion implantation; texturing the catalysts; using two- or multicomponent metal alloys with the optimal catalyst-adsorbate energy bond; using metal + nonmetal compounds; using oxides and other catalysts capable of redox transformations; developing multicomponent oxides with a high current exchange in the end reaction; developing catalysts' surfaces; and modifying catalyst surfaces with adatoms. Titanium, nickel, lead, and carbon materials are the main materials presently used to manufacture anodes. Catalytically active coatings are made mainly from platinum and its alloys, nickel and its alloys, and oxides of the platinum metals, cobalt, nickel, iron, titanium, manganese, tin, and lead. Anodes to be used in electrolysis must have a low main-reaction overvoltage. Corrosion-resistant metals may be used for reactions occurring at low anode potentials. The requirements regarding cathode materials are less rigid than those set for anode materials because anodic dissolution of catalysts and carriers is not stimulated at the cathode. Cathode electrocatalysts can still chemically dissolve and corrode (thus absorbing oxygen and releasing hydrogen), however. Fuel elements with alkaline, solid-polymer, and phosphoric acid electrolytes and high-temperature fuel elements have recently been developed and tested, and three types are currently being used in actual practice. Electrocatalysts have already found use in air-zinc polymer electrodes in which reduction of the oxygen of air is accelerated by activated charcoal. The use of catalytically active electrodes is becoming increasingly widespread; for example, a reversible hydrogen electrode activated by platinum (10 to 40 g/m<sup>2</sup>) has been developed for use in a nickel-hydrogen alkaline battery for use in space. Alkaline electrolyzers are the principal water electrolyzers in use at the present time. In first-generation electrolyzers, nickel-plated steel sheets are used at the cathode, whereas nickel-plated steel is used at the anode. Second-generation and newly developed electrolyzers have electrodes with more active catalysts such as porous nickel, Raney nickel, nickel surface skeletal catalysts, and nickel-molybdenum alloys. The production of chlorine, chlorine-oxygen compounds, peroxides, and manganese dioxide is another area in which electrocatalysts are being used. Electrochemical techniques are also being used to extract zinc, chromium, manganese, cadmium, cobalt, and other metals from aqueous solutions at a cathode. The process is implemented with insoluble anodes and with either silver-doped lead dioxide or MnO<sub>2</sub>/Ti serving as the catalyst of oxygen release. The following electrochemical methods of treating natural waters and sewage have also come to enjoy extensive use in recent years: electrocoagulation, electrodialysis, electroflotation, electrocorrection of pH and potential, electrooxidation, and electrodeaeration. Figures 8, tables 4; references 94: 76 Russian, 18 Western.

**The Production and Properties of Palladium Deposits on Carbon Fabric**

937M0147D Moscow ELEKTROKHIMIYA in Russian  
Vol 29 No 4, Apr 93 pp 465-468

[Article by Shigan Lu, Ye. A. Kolyadko, and B. I. Podlovchenko, Moscow State University imeni M. V. Lomonosov; UDC 541.135.5:546.98]

[Abstract] A study examined the possibility of applying palladium onto type ULSH carbon fabric (specific surface,  $970 \text{ m}^2/\text{g}$ ; average pore diameter,  $\approx 4.4 \text{ nm}$ ) by electrodeposition and impregnation. Before the palladium was applied to it, the carbon fabric was subjected to anode-cathode polarization at potentials of 1.0 and 0.0 V for 30 minutes with replacement of the background solution ( $0.5 \text{ M H}_2\text{SO}_4$ ). The palladium was dispersed onto the carbon fabric's surface by either impregnation or electroprecipitation from a solution of  $0.1 \text{ M PdCl}_2 + 0.5 \text{ M H}_2\text{SO}_4$ . The fabric specimens to be impregnated was first subjected to preliminary anode-cathode activation and then held in an electrolyte solution with a potential of 0.13 V. After the electrode's potential had stabilized, the background solution was replaced by a solution containing palladium ions. After the potential shifted to the anode side and reached about 0.7 V, the solution was drained out and hydrogen passed through the cell for about three hours. The cell was refilled with background solution, and the electrode's potential was brought to 0 V by blowing hydrogen through. The electrodeposition of palladium was performed under potentiostatic conditions at potentials of 0.40, 0.50, and 0.58 V. Copper adatoms were used to study the processes of hydrogen adsorption and absorption. In the presence of a single layer of copper adatoms on the Pd/C electrodes in the hydrogen range of potentials, a sharp drop in electrode polarization capacity was observed. It was linked to the decrease in the amount of adsorbed hydrogen when the copper adatoms were absorbed. A correlation was found between the concentration of hydrogen in the  $\alpha$ -phase Pd(H) and dispersion of the palladium. The following slope coefficient values were found for Pd/C electrodes: -156 mV for the electrode produced by impregnation and -172 mV for the electrode produced by electrodeposition at a potential of 0.4 V. Figures 4, table 1; references 22: 4 Russian, 18 Western.

**Intensifying Process of Hydrogen Transfer to Palladium Membrane**

937M0147E Moscow ELEKTROKHIMIYA in Russian  
Vol 29 No 4, Apr 93 pp 490-496

[Article by I. I. Kolesnichenko, A. A. Michri, and A. G. Pshenichnikov, Electrochemistry Institute imeni A. N. Frumkin, Russian Academy of Sciences, Moscow; UDC 541.135.5]

[Abstract] The kinetic laws governing the individual stages of the process of hydrogen transfer through a palladium membrane were studied in an attempt to develop methods of accelerating the process' slow stages. The process studied included five sequential stages: formation of adsorbed hydrogen on the contact side; transition of the adsorbed hydrogen to an absorbed state; diffusion transfer of the hydrogen in the bulk of the metal; transition of the absorbed hydrogen to an adsorbed state on the diffusion side; and oxidation of the adsorbed hydrogen. All of the experiments were conducted either in a conventional three-section cell on an electrode immersed in an electrolyte or else in a two-chamber cell that had a membrane pressed between its chambers. All solutions were prepared by diluting concentrated ultrapure sulfuric acid with twice-distilled water. Solution purity was controlled by the effect of suppression by impurities of the hydrogen adsorption/absorption maxima on the platinum electrode. The palladium's true surface was determined from the amount of oxygen desorbed from the surface during the course of the anode-cathode potentiodynamic pulses. The potentials were measured relative to a reversible hydrogen electrode in the same solution. The kinetic parameters of the injection/extraction processes were measured on immersed electrodes (palladium foil  $20 \mu\text{m}$  thick) containing a specified amount of dissolved hydrogen that was determined by the equilibrium potential. The experiments established that in the range of the existence of the  $\alpha$ -phase, the current density referenced to the true surface ( $j_0$ ) remains practically constant. In the range of the  $\beta$ -phase, on the other hand,  $j_0$  increases as the potential shifts to the cathode side. Increasing the surface roughness on the contact side while keeping the exchange current constant and introducing promoters (Pt, Rh) were both found to increase hydrogen permeability. On the basis of these findings a method was developed for coating a palladium surface with a highly adhesive stable electrocatalytic coating that would increase the rate of mass transfer through a membrane by more than an order of magnitude. Figures 14; references 11: 6 Russian, 5 Western.

### The Electron Heat Capacity of Superconductors With an Intermediate Link

937M0145A Moscow SVERKHPROVODIMOST: FIZIKA, KHIMIYA, TEKHNIKA in Russian Vol 6 No 1, Jan 93 pp 1-23

[Article by A. P. Zhernov, Kurchatov Institute Russian Scientific Center, Moscow, and E. P. Chulkin, Moscow Physics Engineering Institute]

[Abstract] The electron heat capacity of superconductors with an intermediate link is examined. The effect that a delay in the attractive interaction has on the low-temperature behavior and magnitude of the jump in electron heat capacity close to the critical temperature ( $T_c$ ) of the transition to superconductivity is analyzed. It is shown that experimental data regarding the deviation from the Bardeen-Cooper-Schrieffer theory may be used to estimate the key parameters of the spectrum of an attractive interaction. The suppression of the said jump owing to paramagnetic defects in the case of high and low concentrations of defects is also examined. Specifically, it is shown that when the concentration of paramagnetic defects is increased, the magnitude of the jump in electron heat capacity decreases much faster than  $T_c$  changes. Making corrections in  $\Delta C_e$  on account of an intermediate link helps to intensify the differences in the behaviors of  $\Delta C_e$  and  $T_c$ . The roles of weak and strong fluctuations are examined qualitatively. In the case of a weak link, the value obtained for the jump in normalized units is half the classical value. For superconductors with an intermediate link owing to delay effects, the drop in the magnitude of the jump is compensated to a certain degree. For high-temperature superconductors with a link value ( $\lambda$ ) between 1 and 2, this compensation may be virtually complete. In the case of layered superconductors, there is a hierarchy of fluctuation phenomena. As the critical temperature is approached, weak two-dimensional fluctuations are replaced by strong two-dimensional fluctuations. Only in direct proximity to  $T_c$  do strong three-dimensional fluctuations appear. According to the results presented for new superconductors, the magnitude of the jump in electron heat capacity may be close to the classic weak-link theory result through mutual compensation of the contributions made by delay and strong fluctuations to  $\Delta C_e$ . References 32: 13 Russian, 19 Western.

### Paramagnetism and Superconductivity in the Hubbard Model With Strong Repulsion

937M0145B Moscow SVERKHPROVODIMOST: FIZIKA, KHIMIYA, TEKHNIKA in Russian Vol 6 No 1, Jan 93 pp 24-36

[Article by R. O. Zaytsev, Kurchatov Institute Russian Scientific Center, Moscow]

[Abstract] The phenomenon of short-acting repulsion for electrons with oppositely directed spins leading to a significant increase in paramagnetism has been studied with an extremely low electron concentration and for the

three-dimensional case. Because this parameter increases rapidly as the concentration increases, an extremely strong increase in paramagnetic susceptibility and even the possible appearance of ferromagnetism were hypothesized. It later turned out that as the energy of relative motion increased, the amplitude of two-particle scattering moderated, remaining positive, and then changed sign, continuing to moderate with an increase in Fermi energy. This phenomenon, which is an analogue of the Ramsauer effect in a lattice, is examined herein in a Born approximation for a Hubbard model with infinite repulsion. The tunnel Hamiltonian is expressed through Hubbard  $X$ -operators and then rewritten through "ordinary" creation and destruction operators. The exact amplitude of scattering in an empty square lattice is calculated; this makes it possible to find the magnetic permeability at the gas limit (when  $T = 0$ ) where the influence of the effects of scattering is most significant. An attempt is made to calculate the magnetic permeability for all concentrations of hole excitations. The critical concentration at which (when  $T = 0$ ) the system acquires Cooper instability and makes the transition to a state of superconductivity is determined in a logarithmic approximation. The main result of the analysis performed is said to be that the strong increase in Stoner's factor for spin paramagnetic susceptibility is largely determined by the energy dependence of the amplitude of two-particle scattering. In cases of a slowly changing state density, paramagnetic susceptibility diminishes as the Fermi energy increases. A further increase in the energy of relative motion results in a change in the sign of the scattering amplitude so that beginning at some concentration, the system moves into a state of superconductivity. The analysis results are found to be qualitatively consistent with the phase diagram of  $PdH_x$ . An analysis is appended that demonstrates that the results presented in this article, which have been obtained in a ladder approximation, do not undergo any qualitative changes if the analysis is conducted in a parquet approximation. Figures 2; references 10: 6 Russian, 4 Western.

### Possible Nature of the Electron Spectrum and Conductivity of Doped Fullerite

937M0145C Moscow SVERKHPROVODIMOST: FIZIKA, KHIMIYA, TEKHNIKA in Russian Vol 6 No 1, Jan 93 pp 37-43

[Article by M. A. Ivanov, Metal Physics Institute, Ukraine Academy of Sciences, Kiev, V. M. Loktev, Theoretical Physics Institute imeni N. N. Bogolyubov, Ukraine Academy of Sciences, Kiev, and V. S. Ostrovskiy, Physics Institute, Ukraine Academy of Sciences, Kiev]

[Abstract] An "impurity" model of the formation of the electron spectrum of fullerite doped with atoms of selected alkaline metals ( $A_xC_{60}$ ) is proposed. The model presupposes the hybrid nature of the states in its conduction band. The proposed model is used as a basis for explaining why the metal-insulator transition in the

study system occurs only in the vicinity of  $x = 3$ . Figure 1; references 18: 8 Russian, 10 Western.

### Raman Scattering of Light on Phonons in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ Crystals With Selective Substitution of Isotopes

937M0145D Moscow SVERKHPROMODIMOST:  
FIZIKA, KHIMIYA, TEKHNIKA in Russian  
Vol 6 No 1, Jan 93 pp 58-63

[Article by Ye. Ya. Sherman, Moscow Physics and Technology Institute, Dolgoprudny, Moscow Oblast]

[Abstract] A study examined the Raman scattering of light on phonons in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  crystals with selective substitution of oxygen isotopes. The primary objectives of the study were to determine exactly how selective isotope substitution is expressed in Raman scattering spectra and to assess the possibilities of obtaining information from experimental results regarding the structure of the crystal lattice and its electron properties. The analysis is based on the premise of the mixing of fully symmetrical modes. According to this premise, in high-temperature superconductors, all oxygen ions permitted by the system's symmetry participate in high-frequency ( $\geq 300 \text{ cm}^{-1}$ ) oscillations of the crystal lattice, which is to say that all oscillations of one symmetry are highly "mixed" with one another. Two different substitutions are examined individually, i.e., substitution of the plane ions (the crystal  $\text{YBa}_2\text{Cu}_3^{18}\text{O}_{4-16}\text{O}_{3-x}$ ) and substitution of bridge oxygen (O4) (the crystal  $\text{YBa}_2\text{Cu}_3^{18}\text{O}_2^{16}\text{O}_{5-x}$ ). Even slight decreases in phonon mode frequency are found to result in a significant change in the scattering pattern. Changes occur in both the frequencies of all fully symmetrical modes and their intensities. There are a number of problems regarding attempts to determine crystal lattice parameters from experiments. In the case of substitution of plane oxygen ions in the crystal  $\text{YBa}_2\text{Cu}_3\text{O}_6$ , for example, the difference in mode frequencies is so small that the frequencies cannot be experimentally separated. A set of six variables (frequency and ratio of the intensities of fully symmetrical modes before and after isotope substitution) may eventually be used to obtain all of the coefficients used in the Lagrangian that marks the starting point of the analysis presented as well as the ratio of the contributions of different electron transitions to the formation of scattering intensity. A complete set of such data for the aforementioned crystals does not currently exist, however. Figures 2; references 5: 4 Russian, 1 Western.

### Optical and Electrical Properties of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ Monocrystals

937M0145E Moscow SVERKHPROMODIMOST:  
FIZIKA, KHIMIYA, TEKHNIKA in Russian  
Vol 6 No 1, Jan 93 pp 71-81

[Article by L. V. Nomerovannaya, A. A. Makhnev, M. M. Kirillova, S. V. Moshkin, A. I. Ponomarev, and V. A.

Kostylev, Metal Physics Institute, Ural Department, Russian Academy of Sciences, Yekaterinburg]

[Abstract]  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  monocrystals containing three different amounts of oxygen were studied. The three specimen crystals were found to have characteristic temperatures of the transition to superconductivity ( $T_c$ ) of 62, 85, and 63 K, respectively. The variance of their complex dielectric constant in the energy range from 100 meV to 5.0 eV was determined by the ellipsometric method. The crystals' optical properties were measured by the polarimetric method at room temperature. The temperature dependence of their electrical resistance and the Hall effect was measured by the Van der Pol method. Measurements of the values of the charge carriers' plasma frequencies revealed that the plasma frequency changes very slightly as stoichiometry with respect to oxygen is changed. The carriers' effective masses were estimated: As the number of carriers decreased from  $6.2 \times 10^{21}/\text{cm}^3$  to  $0.5 \times 10^{21}/\text{cm}^3$ , their effective mass varied from 5 to 0.5. The spectra of the optical conduction of monocrystals of the system  $\text{YBa}_2\text{Cu}_3\text{O}_{6-x}$  and  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  were compared as their oxygen content was varied. The evolutions of the optical absorption spectra for both systems as the number of carriers in them was changed were found to be remarkably similar on six counts: 1) as the number of carriers increases, there is a redistribution of electron states from high- to low-energy states; 2) reducing the number of carriers results in a sharpening of the absorption edge at 1.5 to 1.7 eV; 3) an increase in oxygen deficit leads to a sharp increase in the intensity of interband structures at 5.1 eV in the system 123 and at 3.7 eV in the system 2212; 4) the change in contribution to  $\sigma(\omega)$  is due not to the plasma frequency but rather to the relaxation frequency ( $\gamma$ ); 5) the similarity of the energy position and the shape of the absorption band in the mid-IR region confirms the presence of low-energy band gaps in the spectra of both classes of materials; and 6) the individuality of the  $\sigma(\omega)$  spectra in the range from 100 meV to 5 eV for Bi and Y systems with similar numbers of carriers is manifested only in additional absorption at 2.5 to 4 eV in Bi cuprates (which are associated elsewhere with Bi-O states). Figures 4, table 1; references 26: 7 Russian, 19 Western.

### Distinctive Features of the Josephson Effect in a Y-Ba-Cu-O Bridge in Magnetic and Microwave Fields

937M0145F Moscow SVERKHPROMODIMOST:  
FIZIKA, KHIMIYA, TEKHNIKA in Russian  
Vol 6 No 1, Jan 93 pp 82-90

[Article by M. A. Zelikman, St. Petersburg State Technical University, St. Petersburg, A. S. Katkov and V. I. Krzhimovskiy, All-Union Scientific Research Institute of Metrology imeni D. I. Mendeleyev Scientific Production Association, St. Petersburg, and S. V. Kozyrev and V. V. Tretyakov, Physics Engineering Institute imeni A. F. Ioffe, St. Petersburg]

**[Abstract]** An experiment was performed to study the characteristic features of stationary and nonstationary Josephson effects in a Y-Ba-Cu-O bridge in magnetic and microwave fields. A bridge about 0.1 mm long was formed (by scrubbing) in a Y-Ba-Cu-O ceramic wafer measuring 2 x 3 x 10 mm. The wafer was then placed in an external constant magnetic field created by a solenoid measuring 18 mm in diameter and 8 mm in length and consisting of 100 turns of wire 0.1 mm in diameter. The coil had a calculated constant of 60 G/A. Microwave energy of 8-9 GHz was fed to the bridge through a matching impedance transformer. The experiment was performed on a unit (described elsewhere) containing a frequency-stable microwave generator, volt-ampere characteristic recording system, and N306 graph plotter. The magnetic field was found to result in the creation of a constant "induced" current through the contact, which in turn resulted in volt-ampere characteristic asymmetry. In the stationary case, this entailed the occurrence of a constant voltage on the contact when an alternating current with an amplitude greater than that of the critical current was passed through it. In the nonstationary case and in the presence of microwave irradiation, the volt-ampere characteristic of a contact containing a Shapiro step may intersect the voltage axis at a nonzero point with a zero external current depending on  $B_e$ . The intersection of the first and second steps with the  $I$ -axis was fixed experimentally when  $I = 0$ . The magnitude of the displacement of the center of the volt-ampere characteristic along the current axis observed in the experiment was found to be quasi-periodically dependent on the magnetic and microwave fields, and the voltage value may be quantized in accordance with Josephson's equation. The occurrence of an "induced" current was explained within the framework of a model in which a bridge is considered to be an asymmetrical loop with weak links (i.e., a loop with two Josephson contacts). In an external magnetic field, the condition of quantization of the fluxoid in the loop results in the occurrence of a circulating current that in cases of asymmetry of the "inductances" of the loop's arms, may be looked upon as an equivalent constant displacement current. Figures 6; references 15: 8 Russian, 7 Western.

### Structural Instability and Transport Properties in the System $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$

937M0145G Moscow SVERKHPROMODIMOST  
FIZIKA, KHIMIYA, TEKHNIKA in Russian  
Vol 6 No 1, Jan 93 pp 91-97

[Article by Yu. S. Bulyshev, S. V. Serykh, M. P. Sushko, and A. G. Shneyder, Scientific Research Institute of Applied Physics, Irkutsk University, Irkutsk]

**[Abstract]** A study examined structural instability and transport properties in the system  $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$  with a wide range of Ba impurity concentrations ( $0.02 \leq x \leq 0.40$ ). The study specimens were produced by a solid-phase synthesis process that included annealing a mixture of starting compounds ( $\text{La}_2\text{O}_3$ ,  $\text{BaCO}_3$ , and  $\text{CuO}$ ) for 20 hours at 900°C, pulverizing the resultant mixture

and molding it into tablets, sintering them at 1,000°C for 40 hours, annealing them at 700°C for 70 hours, and cooling them inside the furnace. X-ray phase analysis on a DRON-3M diffractometer indicated that the specimens with  $x \leq 0.2$  were practically single-phase compounds, whereas those with  $x = 0.3$  and 0.4 contained from 10 to 15 wt.-% impurity phases. The usual methods were used to measure the temperature dependences of the resistance and thermoelectromotive force of  $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$  specimens with different levels of Ba impurities. The measurement results were used to plot  $c(x)$ ,  $S(x)$ , and  $T_c(x)$  phase diagrams. The dependences of the parameter  $c$  of the elementary cell  $c(x)$  and the critical temperature of the transition to superconductivity  $T_c(x)$  obtained from the thermoelectromotive force data were found to manifest anomalies near the point of the structural phase transition from an orthorhombic to a tetragonal phase. The thermoelectromotive force sign change close to  $T_c$  was linked to the inhomogeneity of the phase composition of specimens with an impurity concentration in the range  $x = 0.10$  to 0.20. The concentration dependence of thermoelectromotive force at room temperature  $S(x)$  determined in the experiment was consistent with estimates obtained by using a Hubbard model in the high-temperature limit with consideration for the disorder of the impurity. Figures 5; references 22: 1 Russian, 21 Western.

### Charge and Energy Distributions of Particles Sputtered From Y-Ba-Cu-O and Bi-Sr-Ca-Cu-O High-Temperature Superconductors

937M0145H Moscow SVERKHPROMODIMOST  
FIZIKA, KHIMIYA, TEKHNIKA in Russian  
Vol 6 No 1, Jan 93 pp 111-120

[Article by A. B. Popov, S. B. Kablukov, B. N. Makarenko, A. Yu. Fisher, and A. P. Shergin, Physics Engineering Institute imeni A.F. Ioffe, Russian Academy of Sciences, Saint Petersburg]

**[Abstract]** The exits and energy spectra of secondary neutral and charged particles sputtered out during ion bombardment of the ceramics  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  ( $T_c \approx 95^\circ\text{C}$ ) and  $\text{Bi}_{1.82}\text{Sr}_{1.73}\text{Ca}_{1.25}\text{Cu}_{2.2}\text{O}_x$  ( $T_c \approx 95^\circ\text{C}$ ) were measured.  $\text{Ar}^+$  ions with an energy of 5.5 keV and a current density on the specimen of  $10 \mu\text{A}/\text{cm}^2$  was used as the primary beam. The angle of incidence of the primary ions was 50°, and the exit angle of the analysis particles was 90° relative to the surface. The bombardment was performed in a vacuum of  $1 \times 10^{-5}$  Pa. An electron beam with an energy of 100 eV, current of 1 mA, and cross section of  $4 \times 5 \text{ mm}^2$  guaranteed effective ionization of the sputtered atoms at the  $10^{-4}$  to  $10^{-5}$  level. A correlation was established between the magnitude of surface binding energy and the arrangement of the atoms in the crystal lattice. The structure of the charged particles' mass spectra was found to correspond to the crystal-chemistry structure of high-temperature superconductor materials. In the case of oxygen, the yields of neutral and negative charged components were comparable, which is in sharp contrast with the sputtering of metal atoms. In

the case of Y<sup>+</sup>, Ba<sup>+</sup>, Cu<sup>+</sup>, Sr<sup>+</sup>, and Ca<sup>+</sup> positive ions, an exponential dependence of the degree of ionization on the atoms' ionization potential was discovered. Electron exchange mechanisms were determined to play a decisive role in the formation of secondary ions. Figures 4; references 22: 13 Russian, 9 Western.

### Characteristic Features of the Laser Desorption of Oxygen From a Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8</sub> Monocrystal Near T<sub>c</sub>

937M0145I Moscow SVERKHPROVODIMOST: FIZIKA, KHIMIYA, TEKHNIKA in Russian  
Vol 6 No 1, Jan 93 pp 121-125

[Article by P. O. Artamonov and A. A. Lisachenko, Physics Scientific Research Institute, St. Petersburg]

[Abstract] Time-of-flight spectroscopy was used to study the kinetic energy distribution of oxygen desorbed from a Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8</sub> monocrystal subjected to pulsed radiation from an LTIPCh-5 laser ( $\tau = 15$  ns;  $\lambda = 1.064$  nm; P/S  $\approx 2\text{-}4$  mW/cm<sup>2</sup>). Bi(2212) monocrystals ( $T_c = 85$  K) were used in the experiments, which were performed under conditions of an ultrahigh vacuum ( $p \approx 2 \times 10^{-10}$  torr). The time-of-flight spectra obtained were found to contain two components with very different average kinetic energy values for the molecules: a "fast" form with  $T_{maxw} = 3,000$  to 4,000 K and a "slow" form with  $T_{maxw} = 350$  to 360 K. The parameters of the time-of-flight spectra included a jump discontinuity at the point of passage through  $T_c$ . Unlike in Y(123), in which only the "fast" form has been observed at the temperature of liquid nitrogen and only the "slow" form has been observed at  $T = 300$  K, in the Bi(2212) monocrystals studied both forms coexist in both temperature intervals. A model of the formation of both components of desorbed oxygen was proposed in which desorption is considered the result of the interaction of surface anion radicals of oxygen (atomic or molecular) with photogenerated holes. The discontinuity in the parameters of the time-of-flight spectra that has been detected previously in a Y(123) monocrystal but not observed in other oxides (TiO<sub>2</sub>, ZnO, Al<sub>2</sub>O<sub>3</sub>, etc.) was linked to the formation of Cooper pairs. Figures 4; references 11: 6 Russian, 5 Western.

### Ohmic Contacts to a Y<sub>1</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub> Oxide Superconductor Produced by the Silver Foil Electroexplosion Method

937M0145J Moscow SVERKHPROVODIMOST: FIZIKA, KHIMIYA, TEKHNIKA in Russian  
Vol 6 No 1, Jan 93 pp 128-135

[Article by O. N. Alifertsev and V. P. Snesarevskiy, Electronic Engineering Materials Scientific Research Institute, Kaluga]

[Abstract] A study examined the possibility of using the method of the electroexplosion of silver foil to produce relatively low ohm metal contacts ( $\rho_c = 10^{-5}$  to  $10^{-6}$

$\Omega\text{-cm}^2$  at 77.4 K) for various high-temperature superconducting materials (epitaxial films and ceramics). A small laboratory unit was developed to implement the proposed process. The unit made it possible to reach explosion product flow speeds of 1 km/s. After varying the process variables (explosion energy, foil thickness, dose of explosive, and length and diameter of the gas-dynamic nozzle), the researchers succeeded in producing high-temperature superconductor/Ag structures with the following parameters:  $h = 10$   $\mu\text{m}$ ;  $d = 0.1$  cm;  $l = 10$   $\mu\text{m}$  (film); and  $l = 30$   $\mu\text{m}$  (ceramic). These structures were capable of correctly measuring contact resistance at 77.4 K on the order of  $10^{-8}$  in the case of epitaxial films and  $10^{-6}$  in the case of ceramics. During the course of the measurements, the density of the current through the contact did not exceed tens of amperes per square centimeter. Subsequent annealing of the structures in an oxygen flow at a temperature of 500°C for 30 minutes did not result in any marked change in  $\rho_c$ . There are plans for further studies to improve the new silver foil electroexplosion process and obtain lower  $\rho_c$  by optimizing the nozzle material and geometry and the medium in which the contact is applied and by pretreatment of the high-temperature superconductor specimens. The new process was found to be simple and fast and is characterized by a high contact material transfer coefficient (75-80%). Figures 2, tables 3; references 24: 12 Russian, 12 Western

### Electrolytic Oxygen Saturation of Y-Ba-Cu-O Ceramics in Solutions and Their Resistometric Characteristics

937M0145K Moscow SVERKHPROVODIMOST: FIZIKA, KHIMIYA, TEKHNIKA in Russian  
Vol 6 No 1, Jan 93 pp 144-158

[Article by V. D. Kalugin, V. N. Yasko, N. S. Opaleva, and L. Yu. Voronko, Chemistry Scientific Research Institute, Kharkov State University, Kharkov]

[Abstract] A series of electrochemical studies were performed on two groups of specimens of Y-Ba-Cu-O 123 ceramic. The specimens in the first group all had an initial oxygen deficiency. The specimens in the second group had "lost their oxygen stoichiometry" while in use. The following solutions were used: aqueous solutions of NaOH in different concentrations: 0.25 M NaOH in a solvent mixture (C<sub>2</sub>H<sub>5</sub>OH + H<sub>2</sub>O); a mixture of 0.25 NaOH and CH<sub>3</sub>CN and H<sub>2</sub>O; and CH<sub>3</sub>CN-based solutions with additives of salicylic acid, copper palmitate, and water. Electrolytic copper was used as the cathode, and the working electrodes for the polarization measurements consisted of 40 to 70- $\mu\text{m}$ -thick Y-Ba-Cu-O ceramic coatings applied to MgO substrates (the ceramic specimens were annealed in air at 950°C and cooled for 14-16 hours). Electrolytic oxygen oversaturation was studied in YBa<sub>x</sub>Cu<sub>3</sub>O<sub>7</sub> specimens with  $6.0 < x \leq 6.5$ . Resistometric measurements established the following effects: electrolytic oxygen saturation of both thin-layer and bulk specimens of the study ceramic; fixation of electrolytic oxygen in the lattice of the oxide mix during

annealing; and acquisition (or recovery) of superconductivity properties by the study specimens in liquid nitrogen. Recovery of lost (or absent) oxide components by the study specimens was found to take place in the stage of electrolytic oxygen saturation. It was found to occur in the solid phase at potentials less positive than the potential of oxygen evolution. The experiments also confirmed the researchers' hypothesis regarding the conversion of all chemical forms of yttrium, barium, and copper compounds into higher oxides and confirmed the presence of oxygen adsorbed by the ceramic's bulk. The studies thus demonstrated that anodic electrochemical treatment of yttrium ceramic in solutions helps to boost the efficiency of high-temperature annealing in an oxygen-containing atmosphere to reduce oxygen deficiency resulting from degradation. Figures 5, tables 4; references 19: 6 Russian, 13 Western.

#### **Phase Relationship in a $\text{BaCu}_3\text{O}_4$ - $\text{Y}_2\text{Cu}_3\text{O}_6$ Polythermal Section and Projection of the Liquidus Surface of the System Y-Ba-Cu-O**

937M0145L Moscow SVERKHPROMODIMOST:  
FIZIKA, KHIMIYA, TEKHNIKA in Russian  
Vol 6 No 1, Jan 93 pp 159-166

[Article by A. I. Sechnoy, G. A. Mikirticheva, V. I. Shitova, S. K. Kuchayeva, L. Yu. Gabovenko, and R. G. Grebenshchikov, Silicate Chemistry Institute, Russian Academy of Sciences, St. Petersburg]

[Abstract] The phase relationships existing in a  $\text{BaCu}_3\text{O}_4$ - $\text{Y}_2\text{Cu}_3\text{O}_6$  polythermal section were analyzed in air at temperatures ranging from 900 to 1,400°C. The triangulation performed with the system Y-Ba-Cu-O in a subsolidus area of the aforesaid section established three triphase fields:  $\text{BaCuO}_2$ - $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ - $\text{CuO}$ ;  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ - $\text{Y}_2\text{BaCuO}_5$ ; and  $\text{Y}_2\text{BaCuO}_5$ - $\text{Y}_2\text{Cu}_2\text{O}_5$ - $\text{CuO}$ . The high-temperature part of the system was found to be characterized by phase relationships of the eutectic and peritectic types that are complicated by the dissociation process of copper-containing compounds. A liquidus surface production in the triangle  $\text{BaCuO}_2$ - $\text{Y}_2\text{O}_3$ - $\text{CuO}$  was constructed on the basis of experimental data for phase relationships in different polythermal sections of the study system. The researchers used the method of determining the compositions of nonvariant points from the intersections of straight lines corresponding to the directions of melt equilibrium crystallization from the peaks of different compounds in an approximation of ideal solutions. The distinguishing feature of this method is the fixing of those compositions on the polythermal sections that correspond to the temperature-concentration boundaries of those phase regions in which only one solid phase is present with the liquid phase. It is this solid phase that determines the direction of the melt's crystallization along the straight line passing through the peak of the given phase in the polyhedron of compositions and through the composition of the given figurative point in

the polythermal section under examination. Figures 3; references 19: 6 Russian, 13 Western.

#### **The Reaction of $\text{YBa}_2\text{Cu}_3\text{O}_6$ With Iodine. 1. Phase Composition of Reaction Products**

937M0145M Moscow SVERKHPROMODIMOST:  
FIZIKA, KHIMIYA, TEKHNIKA in Russian  
Vol 6 No 1, Jan 93 pp 187-198

[Article by A. P. Nemudryy, S. S. Shatskaya, and B. B. Bokhonov, Solid-State Chemistry and Crude Minerals Processing Institute, Siberian Department, Russian Academy of Sciences, Novosibirsk, and I. G. Vasilyeva and N. F. Zakharchuk, Inorganic Chemistry Institute, Siberian Department, Russian Academy of Sciences, Novosibirsk]

[Abstract] The methods of electron microscopy and selective and differentiating dissolution were used to determine the qualitative and quantitative phase composition of the products of the reaction of  $\text{YBa}_2\text{Cu}_3\text{O}_6$  with iodine. Both powder and monocrystalline specimens were studied. The morphological changes that occurred in the monocrystalline  $\text{YBa}_2\text{Cu}_3\text{O}_6$  specimens when they were treated with iodine for varying amounts of time were tentatively divided into several states. First, a thin film of primary reaction product formed on the crystal's surface after 15-30 minutes. Next, the primary reaction product crystallized, resulting in the formation of well-bounded  $\text{CuI}$  crystals. After 3-4.5 hours, these crystals reached 10-20  $\mu\text{m}$  in size. In the third stage, acicular  $\text{BaI}_2$  crystals appeared along with the copper iodide crystals. After  $N,N$ -dimethylformamide was used to remove the barium and copper iodides, a monocrystal surface coated with a network of cracks and thin layer of amorphous product that produced a halo in the electron diffraction patterns was revealed. Analogous results were obtained when powder specimens were used. The iodine-containing copper-deficient  $\text{YBa}_2\text{Cu}_{3-x}\text{O}_y\text{I}_z$  phase produced was determined to be a high-temperature superconductor. The formation of this high-temperature superconducting phase was associated with both the intercalation of the anions ( $\text{O}$  and  $\text{I}$ ) and the deintercalation of the  $\text{Cu}^+$  cations from the  $\text{CuI}$  chains. Figures 6, tables 4; references 30: 9 Russian, 21 Western.

#### **The Reaction of $\text{YBa}_2\text{Cu}_3\text{O}_6$ With Iodine. 2. The Effect of Iodine on the Superconduction Characteristics of Yttrium-Barium Cuprite**

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[Article by A. P. Nemudryy, I. I. Gaynudinov, and Yu. T. Pavlyukhin, Solid-State Chemistry and Crude Minerals Processing Institute, Siberian Department, Russian Academy of Sciences, Novosibirsk]

[Abstract] In an earlier study, the reaction of  $\text{YBa}_2\text{Cu}_3\text{O}_6$  with iodine was found to result in the formation of an iodine-containing copper-deficient

phase, i.e.,  $\text{YBa}_2\text{Cu}_{3-x}\text{O}_y\text{I}_z$ , possessing high-temperature superconductivity properties. This continuation of that study was undertaken to detail the dependences of the structural and superconduction characteristics of the reaction product on the iodine content. The iodine content of the study specimens was varied by varying the amount of time for which the starting 123 specimens were held in iodine. The study  $\text{YBa}_2\text{Cu}_{3-x}\text{O}_y\text{I}_z$  specimens were subjected to chemical analysis by selective dissolution, quantitative determination of their elements in the liquid and solid phases, and x-ray studies on a DRON-3M diffractometer. The specimens' superconductivity was measured on a SQUID-magnetometer in a field of 1.71 Oe. The specimens' iodine content was found to increase over time, reaching 0.57 mol/mol  $\text{YBa}_2\text{Cu}_3\text{O}_{6.2}$  after 12.5 hours of reaction. Most of the iodine went to form barium and copper iodides. The studies established that the resultant phase may be represented as a continuous series of solid solutions with high-temperature superconductor properties. The temperature of the onset of the transition to a state of superconductivity was found to be determined by the final member of the continuous series of solid solutions, i.e.,  $\text{YBa}_2\text{Cu}_{2.6}\text{O}_y\text{I}_{0.2}$ . The quasi-equilibrium composition  $\text{YBa}_2\text{Cu}_{3-x}\text{O}_y\text{I}_z$  was found to form as a result of deintercalation of  $\text{Cu}^+$  and intercalation of the anions (I and O) and to depend on the reaction conditions. Figures 4, table 1; references 8: 5 Russian, 3 Western.

### The State of Silver in $\text{YBaCuO}/\text{Ag}$ Composites

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[Article by S. Yu. Sumarokov, N. I. Shevtsov, V. F. Tkachenko, R. F. Ramakayeva, L. A. Kotok, K. N. Belikov, and A. B. Blank, Monocrystals Institute, Ukraine Academy of Sciences, Kharkov]

[Abstract] Composites containing 5, 10, 15, and 20% (mass) were produced by holding a mixture of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.93}$  and  $\text{AgNO}_3$  powders for 5 hours at 900°C, grinding them, and holding them for an additional 5 hours at 930°C. The resultant powders were treated with a boiling aqueous solution of acetic acid (1:1) until the sediment ceased dissolving. A "nuclear" filter or glass filter was used to separate the sediment (metallic silver and  $\text{CuO}$ ) from the solution. The silver that had passed into the solution was then determined by x-ray fluorescence. Next, an x-ray phase analysis was performed to determine the ionic silver's location in the composites. The study established for the first time that most of the silver in  $\text{YBaCuO}/\text{Ag}$  composites is present in an ionic state and that it is a component of the crystal lattice. The presence of  $\text{Ag}^+$  in the composite was taken as confirmation of the fact that a 123 superconductor is a strong oxidizer of metallic silver and possibly acts as a promoter of oxidation of silver by the oxygen in air. Table 1; references 12: 3 Russian, 9 Western.

**Fullerenes—A New Form of Carbon**

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[Article by Academician Mark Yefimovich Volpin, director, Institute of Elementoorganic Compounds imeni A. N. Nesmeyanov, Russian Academy of Sciences]

[Text] *A fullerene boom is under way in carbon chemistry. More and more new articles on fullerenes—carbon polyhedrons containing from 60 to 110 or more carbon atoms—are appearing in each issue of the leading chemistry and physics journals. Fullerenes are being studied in a number of institutes of the Russian Academy of Sciences—both chemical and physical. Academician M. Ye. Volpin communicated the theoretical and practical accomplishments of this new branch of science at a meeting of the Russian Academy of Sciences Presidium. The article published below is based on this communication.*

One remarkable feature of science is the unpredictability of its development and its discoveries. Despite our plans and projections, suddenly a growth point appears in an unexpected place on a new tree of knowledge. Such a growth point appeared literally before our eyes in carbon chemistry.

Carbon is a unique element capable of forming an enormous diversity of chains, rings, and compounds with multiple carbon-carbon bonds. Life on Earth and the world of synthetic organic chemistry, which has many millions of chemical compounds to its credit, owe their existence to this diversity of carbon structures.

For practical purposes carbon chemistry rests upon two foundations—the two forms of carbon existing in nature (Figure 1 - not provided). By some irony of fate, one of its forms—the diamond—is the hardest substance on Earth, while the other—graphite—is very soft. The diamond is a three-dimensional lattice of carbon atoms joined together by simple single bonds, while graphite is constructed out of two-dimensional planes that are not joined to one another by chemical bonds. These planes appear as lattices made of strong six-member aromatic rings with a carbon-carbon bond ratio of 1.5. By the way, graphite is the stillest form of carbon.

In 1967 A. I. Sladkov and V. V. Korshak synthesized a third allotropic form of carbon—carbin [karbin], consisting of linear rod-shaped carbon molecules (Figure 1 - not provided)—at the Institute of Elementoorganic Compounds of the USSR Academy of Sciences. It seemed as if all structural possibilities of carbon molecules were exhausted at this point. Then suddenly a completely unexpected form of carbon was recently discovered—carbon polyhedrons that have come to be called fullerenes. The best known of them consists of 60 carbon atoms, and it is shaped like a soccer ball. A new branch of carbon chemistry and physics arose at the intersection of quantum and structural chemistry, mathematics, architecture, bionics, space physics and space

chemistry, and the physics of superconductors—quite different branches of knowledge.

If we wish to discuss the prehistory of the discovery, then we should probably begin with the work of the great mathematician Leonard Euler, who was an active member of the Petersburg Academy of Sciences. In the 18th century he developed the theory of polyhedrons and derived his famous formula, according to which the number of vertices, plus the number of faces, minus the number of edges is equal to 2. It followed from this theory that, as an example, you cannot construct a complete polyhedron out of hexagons. But if you take 13 pentagons, you can build various polyhedrons by introducing different numbers of hexagons, and in particular, a polyhedron with 60 vertices. It would consist of 13 pentagons and 20 hexagons.

As it turns out, nature has made wide use of this principle. Living polyhedrons—the Radiolarians, which have a silicon skeleton made of five- and six-membered rings—are an example. This principle of polyhedron structure was applied in 1985 by the famous American architect Richard Buckminster Fuller in the structure of so-called geodesic domes—buildings with a dome structure. The American pavilion at Expo-67 in Montreal possessed this architecture, and a similar structure can be seen in our country in Sokolniki Park. Steel, duralumin or reinforced concrete structures joined together into polyhedrons by Fuller's light touch are now widely used in architecture.

In the 1960s D. Jones suggested the possible existence of the same type of spherical polyhedrons made from carbon. However, the first stage of the scientific history of the new forms of carbon is associated with the early 1970s, when under the guidance of Professor D. A. Bochvar a the Institute of Elementoorganic Compounds, Ye. G. Galpern and I. V. Stankevich began calculating hypothetical carbon structures. Their first paper was published in 1973 in the DOKLADY AKADEMII NAUK SSSR. It presented quantum-chemical calculations for a carbododecahedrane molecule—the carbon analog of a soccer ball (Figure 2 - not provided), and it predicted that the  $C_{60}$  molecule should be stable and that it should possess chemical stability due to its closed electron shell and its aromaticity. To be honest, the article in DOKLADY AKADEMII NAUK SSSR did not attract much attention. Ask any chemist to accomplish the successive synthesis of such a compound, and he will exclaim in horror that an entire lifetime would be too short for this. This is why the prediction of the stability of the  $C_{60}$  molecule was treated as just another free flight of thought, as science fiction.

The next stage in this interesting history is associated with astrophysics. In the 1980s, diffuse absorption lines with a wavelength of around 216 nm were discovered in the spectra of red giants (carbon stars), in the tails of comets and in interstellar dust using highly sensitive spectrometers. The nature of these lines was discussed, and it was suggested that they belong to carbon clusters.

In 1985, two research physicists studying this problem—G. Kroto and R. Smolli [transliterations]—decided to model the conditions existing in carbon stars. They began studying evaporation of graphite in response to high-power lasers at a temperature of around 10,000° in a helium jet. An intensive peak associated in mass with a  $C_{60}$  molecule and another less-intensive peak corresponding to a  $C_{70}$  molecule were revealed in the mass spectra of graphite vapor. Knowing nothing then about the work done by Bochvar's group in Moscow, or about their publication 12 years earlier, Kroto and Smolli independently arrived at the hypothesis that  $C_{60}$  possesses the geometry of an icosahedron—a "soccer ball," while  $C_{70}$  has the geometry of an extended polygon recalling a rugby ball (Figure 3 - not provided). Among the numerous names proposed for this type of molecule, only "buckminsterfullerene," or "fullerene" for short, after the architect Fuller, has taken. The work of Kroto and Smolli, who actually discovered not the substance per se but only a clue to its existence, initiated the hunt for  $C_{60}$ , which was graced with brilliant success 5 years later. And once again astrophysicists spoke the deciding word. In an attempt to model the substance of interstellar dust, in 1990 V. Krechmer and D. Khaffman [transliterations] developed a method of obtaining noticeable quantities of fullerenes by vaporizing graphite electrodes in an electric arc in a helium atmosphere. A red substance that turned out to be primarily a mixture of  $C_{60}$  and  $C_{70}$ , which could then be separated by chromatographic methods, was isolated by extraction with organic solvents from the carbon black that formed as a result of the graphite's vaporization. Soon after, the first device for making fullerenes was started up, and now fullerenes have already become a commercial product, though of course a still very expensive one (from \$2,000 to \$6,000 per gram of pure  $C_{60}$ ), inasmuch as the process of their separation and purification is so laborious.

Then followed a furious flurry of activity in the area of fullerenes. Within a short time the bibliography on this problem exceeded a thousand names. By now, not only have  $C_{60}$  and  $C_{70}$  fullerenes been obtained, but also isolation of higher fullerenes with 76, 78, 82, 84, 90, 96, 102, 106, 110 and more carbon atoms in individual state is being communicated (Figure 4 - not provided). The existence of superfullerenes—unique "molecular nesting dolls" consisting of carbon layers—is hypothesized. Many properties of industrial carbon, carbon black, coke and pig iron are now being explained by formation of fullerene structures. The very first structural studies confirmed the hypothesis that  $C_{60}$  consists of a combination of 12 five-membered and 20 six-membered rings. This fullerene was found to be an extremely strong and thermostable substance that sublimates in a vacuum at 400° and possesses exceptionally interesting physical and chemical properties. In contrast to other allotropic modifications of carbon, it dissolves in organic solvents, and upon evaporation from solution, it is capable of producing films combining some of the semiconductor properties of gallium arsenide and amorphous silicon

(disorder in an ordered structure). Not long after  $C_{60}$  was obtained as a preparation, synthesis of its salts with alkaline metals—fullerites, possessing superconductor properties—was communicated. While the critical temperature for one of these organic superconductors—potassium fullerite—was 10 K, after acquisition of fullerene compounds of rubidium, cesium, thallium and other metals, it increased to 43 K at high critical current values.

The chemical properties of fullerenes and their unique aromaticity are extremely interesting. They both accept and donate electrons easily, acting as unique molecular accumulators of electrons. They possess a high level of unsaturated bonds—that is, a large number of various reagents may be joined to them, in which case the  $C_{60}$  skeleton can be both preserved intact and expanded. It also has the capability not only for donating "external"  $\pi$ -complexes with transition metals, but also for forming totally unusual endoendral compounds (with a metal atom inside a carbon sphere).

The chemistry of fullerenes has been studied chiefly on the basis of the simplest fullerene— $C_{60}$ . It was found that fullerene readily accepts electrons (up to six electrons per molecule) to produce polyanions. The latter can participate in various reactions; for example they can undergo alkylation, which makes it possible to obtain polymethylated fullerenes, the carbon sphere of which is covered by a "coat" of methyl groups (Figure 5 - not provided). On the other hand  $C_{60}$  absorbs free radicals like a sponge. It can attach up to 24 methyl radicals, forming new stable fullerene radicals (Figure 5 - not provided). And its reaction with biradicals is a promising means of obtaining thermostable fullerene-containing polymers. When exposed to oxidizers (even ones like protonic superacids),  $C_{60}$  readily gives up electrons to form polycations, which are in turn capable of reacting to produce polyoxy- or polyalkoxyfullerenes (compounds containing up to 24 alkoxy groups are known). This opens the road to synthesizing various fullerene derivatives, including water-soluble derivatives and polymers. In a number of reactions,  $C_{60}$  behaves as a polyunsaturated compound, attaching fluorine, chlorine, bromine, hydrogen and other molecules. Up to 60 hydrogen atoms can be attached to it to obtain a hydrocarbon framework in which each carbon sphere is bonded with hydrogen. After 60 fluorine atoms are attached, an analog of Teflon is obtained, which can be expected to possess the properties of a superlubricant.

Fullerenes participate in extremely interesting reactions with sources of divalent carbon—carbenes. Thus, a reaction with diphenyldiazomethane led not only to its double bonding with the  $C_{60}$  molecule but also to introduction of carbon into the polyhedron and its expansion to  $C_{61}$  (Figure 5 - not provided). This reactivity opens up unusually interesting possibilities for introducing  $CX_2$  carbene derivatives and their silicon ( $SiX_2$ ), germanium ( $GeX_2$ ) and other analogues into the fullerene skeleton. Fullerenes with an expanded carbon skeleton or their analogues containing elements different from carbon in

their framework may be obtained in this way. On the other hand communications have also appeared reporting formation of molecules in which some part of the carbon atoms are replaced by boron when fullerenes are synthesized using graphite electrodes saturated with boron compounds.

Fullerene compounds with metals are especially interesting. As was noted earlier, alkaline metals readily donate electrons to fullerenes to form salts—fullerites. Compounds of transition metals—ones such as platinum or iridium—react with fullerenes to form “external”  $\pi$ -complexes on the faces of the polyhedron. It has been reported that up to six platinum atoms can participate in such complexes. This now brings us to a totally remarkable type of fullerene compounds—so-called endoendral complexes. The fact is that the  $C_{60}$  carbon sphere (which has an external diameter of around 7 Angstroms) possesses a cavity around 5 Angstroms in diameter. And atoms of other elements may be enclosed in this cavity—lanthanum or yttrium for example (Figure 6 - not provided). However, lanthanum does not exist in atomic form within  $C_{60}$ : It immediately gives up its electrons to the carbon shell and transforms into a lanthanum cation (+3), which floats freely, due to electrostatic interactions alone, within the negatively charged ball. We can say that this is a unique sort of levitation of a metal cation, which can rest both in the center of the ball and closer to some place on its inner surface. Communications have recently appeared reporting that in the case of  $C_{82}$  fullerene, an endoendral complex containing two yttrium atoms together within a spherical carbon molecule can be obtained and isolated. In this connection

mention must be made of the recently stated hypothesis that during the Chernobyl accident, when graphite rods underwent high-temperature breakdown, spherical carbon molecules enclosing radioactive uranium and other metallic atoms could have arisen. Such “radioactive containers” should present a special danger, inasmuch as they can easily penetrate biological membranes.

Summarizing, we should say that the discovery of fullerenes essentially marks a transition to a new stage in organic chemistry. While up until now a large number of organic compounds have been based on a fragment of the flat six-membered ring of the aromatic benzene molecule, with a limited number of possible combinations of substituents and derivatives, following the advent of three-dimensional carbon chemistry the possibility for creating new organic molecules has been increased by several orders of magnitude. Significant practical applications may be anticipated from this chemistry: new superconducting and magnetic materials, semiconductors, power cells and storage batteries, and biologically active substances. An infant has been born before our eyes which is growing, like the giant in the fairy tales, not by days but by hours. And it is very important to support this newborn infant.

In conclusion I would like to cite a statement by the well known American philosopher John Dewey: “Every great success of science has great daring of imagination at its source.” It seems to me that the advent of the new and unusually interesting chemistry and physics of fullerenes is indebted precisely to the great daring of imagination of scientists.

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